PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-355699
(43)Date of publication of application : 26.12.2000

(51)Int.Cl. C11D 17/08
C11D 7/18
C11D 7/50
H01L 21/304

(21)Application number : 11-168269
(22)Date of filing : 15.06.1999

(71)Applicant : PERMELEC ELECTRODE LTD
(72)Inventor : KATO MASAAKI

(54) OZONE-CONTAINING CLEANING LIQUID, PREPARATION THEREOF, AND CLEANING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a cleaning liquid which can effectively carry out cleaning operations, such as cleaning of electronic apparatuses, resist removal, and sterilization of medical instruments, while preventing impurities or a waste liquid from occurring by dissolving an ozon-containing gas in an halogben-containing organic solvent.
SOLUTION: An ozone-containing gas is dissolved in a halogen-containing organic solvent by bubbling the gas through an air-diffusion plate or an air- diffusion ball. In another method, an anode for ozone generation is installed in the anode chamber of an electrolytic cell partitioned into an anode chamber and a cathode chamber by using a diaphragm; and electrolysis is conducted by using a halogen-containing organic solvent as the anode liquid so that an ozone-containing gas generated in the anode chamber is dissolved in the halogen- containing organic solvent as the anode liquid. A fluorine-containing organic solvent is especially suitable as the halogen-containing organic solvent, the use of a perfluorocarbon or a perfluoroether being preferable.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

CLAIMS

[Claim(s)]
[Claim 1] Ozone content purification liquid characterized by dissolving ozone content gas in the organic solvent containing a halogen.
[Claim 2] Ozone content purification liquid according to claim 1 whose halogen is a fluorine.
[Claim 3] Ozone content purification liquid according to claim 1 whose organic solvent containing a halogen is a perfluorocarbon solvent.
[Claim 4] Ozone content purification liquid according to claim 1 which is electronic equipment washing and/or an object for resist removal.
[Claim 5] The manufacture approach of the ozone content purification liquid characterized by blowing ozone content gas into the organic solvent which contains a halogen using an aeration ball, and making it dissolve.
[Claim 6] The manufacture approach of the ozone content purification liquid characterized by obtaining the organic solvent containing the halogen which electrolyzed using the organic solvent which installs the anode plate for ozone generating in the anode plate room of the cell divided at the anode plate room and the cathode room using the diaphragm, and contains a halogen as an anolyte, and dissolved ozone content gas at the anode plate room.
[Claim 7] The resist removal approach characterized by supplying the ozone content purification liquid made to dissolve ozone content gas in the organic solvent containing a halogen to the wafer front face with which the resist was covered, and to rotate, and removing a resist.
[Claim 8] The resist removal approach characterized by immersing the wafer with which the resist was covered and removing a resist, performing ultrasonic irradiation into the ozone content purification liquid made to dissolve ozone content gas in the organic solvent containing a halogen.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the purification approach which uses ozone content purification liquid available as decolorization of the sterilization liquid of medical equipment, such as a penetrant remover of the electronic equipment which can be used for resist removal, washing of a component, etc., and a syringe, and waste water, or an object for water treatment for deordorization, its manufacture approach, and this purification liquid.
[0002]
[Description of the Prior Art] It is observed as an oxidizer powerful [ozone] and clean, and the use as an object for water treatment is increasing from the reasons of that the residue does not remain to processed underwater one as compared with the thing of the chlorine system for which especially a decomposition product is oxygen and is used from the former, ozone not remaining in itself and the problem of a secondary public nuisance not having it quickly [catabolic rate],, either. Thus, in order to generate ozone useful as an oxidizer, an electric discharge method and an electrolytic decomposition process are mainly adopted, and it is obtained from the former as ozone content gas which is the mixed gas of oxygen and ozone. The former electric discharge method has mixing of NOx which is the discharge oxide of mixing of the electrode material for discharge, or the nitrogen in air, and since it is unsuitable as an object for electronic equipment washing of which especially a high grade is required and there are many impurities also as other applications, it is not desirably used on parenchyma as a process of high grade ozone content gas by current.
[0003] The latter electrolytic decomposition process is an approach of manufacturing ozone content gas by the electrolysis of water, and this electrolysis generation ozone content gas can use water as a raw material, can be electrolyzed using the structure ******** SPE mold electrode structure which made these electrode material adhere to the diaphragm of a solid electrolyte (SPE) as an electrode, using a lead dioxide, gold, platinum, etc., and can obtain the ozone which is a water electrolysis product from an anode plate side as mixture with oxygen. Since this electrolysis ozone is manufactured by the liquid system, it is perfect humid gas, and it has the descriptions, such as being obtained by 15% or more of high concentration. When washing an object using this ozone content gas, ozone content gas can be blown into a direct washing object as the candidates for washing are waste water and pool water, and decomposition and sterilization of a harmful impurity can be performed. Moreover, the ozone content gas generated by electrolysis as the candidates for washing are electronic equipment, such as a semiconductor device, is dissolved in high purity waters, such as pure water, and it is used for washing as ozone water (JP,8-13356,B).
[0004] At detailed metal wiring on the silicon substrate which is one process of manufacture of said semiconductor device, a pattern formation process, or the pattern formation process on a LCD glass substrate, a lithography technique is used frequently. The process for which this lithography is used is performed in order of spreading -> baking -> mask exposure -> etching -> resist removal of the resist which consists of the photopolymer of an organic giant-molecule system. Said ozone water is used for washing and resist removal of each semiconductor device,

and is broadly used from the excellency as the oxidizing agent as the object for component washing and the object for resist removal of electronic equipment. In current, the densification of wiring of multilayer-interconnection-izing, narrow-izing of line breadth, etc. progresses quickly, and the number of the processes which use the lithography of a before [product completion] is increasing. There are an approach of removing by etching as the removal approach of the resist used at the process which uses current lithography by plasma ashing, such as the approach of dissolving a resist with the organic system exfoliation liquid only for resist kinds and oxygen, the oxidation-removal approach which uses together the exfoliation liquid of the inorganic system which consists of the elevated-temperature high concentration sulfuric acid and hydrogen peroxide of 120 ** extent.

[0005] as the penetrant remover after this resist exfoliation -- chlorine-based solvents, such as a trichloroethylene, 1 and 1, 1-trichloroethane, tetrachloroethylene, and a methylene chloride, chlorofluocarbon 112, and chlorofluocarbon 113 etc. -- the chlorofluocarbon system solvent and the aromatic series system solvent are used. Furthermore, since these solvents wash after washing combining a ketone system or an alcoholic solvent, after exfoliating a resist, for example with exfoliation liquid, the resist removal approach which washes with said chlorine-based solvent or a chlorofluocarbon system solvent, subsequently washes with a methyl ethyl ketone, an acetone, etc., and is further washed by isopropanol etc. is used.

[0006]

[Problem(s) to be Solved by the Invention] The above-mentioned ozone water is used for almost all the processes of washing of the component for current electronic equipment. Since this ozone water makes it generate using the high grade ozone content gas made to generate with an electrolytic decomposition process, it has the purity to which the purity demand required of electronic equipment washing responds, and the problem has not produced in respect of purity. However, although to be more high-speed not only the maintenance and improvement in a mere cleaning effect but, and to wash is desired from a number of electronic equipment used as the candidate for washing of increments, by the washing approach which uses current ozone water, it cannot be told to this request that it has fully responded.

[0007] Moreover, although excelled, the exfoliation force and a detergency have a handling-problem point in each, and need to use the above-mentioned resist removal approach properly according to a resist kind. That is, there are troubles, such as generating of resist residue, generating of organic system waste fluid, and generating of a thick sulfuric acid, respectively, and with the increment in the process which uses especially lithography in recent years, the amount of waste fluid increases and it is apprehensive about the bad influence to the increase of a burden and living environment to a processing network. Moreover, ** high concentration ozone water cannot be easily obtained by the resist removal or the washing approach by ozone water, catabolic rate is comparatively quick underwater, if temperature is raised in ** ozone underwater for which dissolved ozone is not used effectively to 60 degrees C or more, the catabolic rate of ozone rises, an ozone level falls by the rise of a water vapor pressure, and, as for ** ozone for which is small to removal of the firm organic substance like a resist, and an etching rate is not suitable to it, the trouble are not effective is pointed out. In addition, although purification of washing with purification liquid, such as ozone water, including various kinds etc. is performed, improvement in much more purification effectiveness is desired. This invention aims at offering the purification approach which uses the ozone content purification liquid which can be performed without generating an impurity and waste fluid more effectively [actuation /, such as washing of such electronic equipment, resist removal, and medical equipment sterilization, / various / purification], its manufacture approach, and this purification liquid.

[0008]

[Means for Solving the Problem] It is the ozone content purification liquid characterized by dissolving this invention in the organic solvent which contains a halogen, especially a fluorine for ozone content gas, and this purification liquid is suitable as electronic equipment washing and/or an object for resist removal. This purification liquid can be manufactured by electrolysis generation of the ozone which uses as an anolyte the organic solvent in which blow ozone content gas into the organic solvent which contains a halogen using an aeration ball, and it is

made to dissolve, and which is caused especially or contains a halogen. It can manufacture efficiently by the dip coating accompanied by the spin cleaning method or ultrasonic irradiation which uses **** purification liquid.

[0009] This invention is explained to a detail below. The ozone content purification liquid concerning this invention which is made to dissolve ozone content gas in the organic solvent containing a halogen, and changes has the following descriptions.

** the solubility to the organic solvent of ozone is markedly alike from the solubility to water, and since it is high, washing capacity becomes high as purification liquid, especially a penetrant remover.

** Since purification capacity is in the organic solvent containing a halogen itself, improvement in still much more purification capacity can be attained.

** If selection of an organic solvent, especially the boiling point are chosen suitably, with ozone water, washing, sterilization, etc. exceeding 100 ** which cannot be performed at temperature will be attained, it can respond conventionally to washing of a broad class including washing which could not be set as the object of ozone washing, and purification of various classes other than washing or sterilization will respond further.

** Since the ozonolysis in the inside of an organic solvent cannot advance easily from an underwater ozonolysis, the life as purification liquid becomes long.

[0010] There are a fluorine, chlorine, a bromine, and iodine as a halogen of the organic solvent which contains an usable halogen by this invention, especially, use of a fluorine and chlorine is desirable and use of a fluorine is the optimal. It is because it can be used repeatedly, without the organic solvent with which the thing with desirable organic solvent which contains a fluorine as an organic solvent containing the halogen of this invention, especially solvent of a perfluorocarbon compound contains a fluorine hardly reacting with ozone, but being maintained by stability in down stream processing of an object purification object, and performing playback etc., and if a perfluorocarbon compound is used, much more improvement in resistance can be attained. The solvent which reacts with ozone, and decomposes or deteriorates is in the organic solvent containing chlorine, a bromine, or iodine, and since contamination by the decomposition product is also considered, to use the organic solvent containing halogens other than a fluorine, it is necessary to choose in consideration of reactivity with ozone.

[0011] Furthermore, as for the organic solvent of this invention, it is desirable that it is a liquid near a room temperature, for example, it is desirable that the boiling point is 30 degrees C or more, and the melting point is an organic solvent 20 degrees C or less. If the boiling point chooses the organic solvent exceeding 100 **, as above-mentioned, with ozone water, washing at impossible temperature etc. will be attained and purification actuation of washing of the member which needs advanced washing which could not be accomplished etc. will be attained by the conventional ozonization. An independent compound or mixture is sufficient as this organic solvent, and it may contain two or more sorts of halogens. When the organic solvent of the desired boiling point cannot be found out, two or more organic solvents are mixed and seen, and the upper boiling point can be adjusted.

[0012] As the organic solvent of this invention, especially an organic solvent containing a fluorine Perfluorocarbon (PFC, compound which permuted all the hydrogen of a hydrocarbon with the fluorine), The perfluoro ether (compound which permuted all the hydrogen of PFE and the hydrocarbon system ether with the fluorine), Hydrochlorofluorocarbon (HCFC, compound which permuted a part of hydrogen of a hydrocarbon with chlorine and a fluorine), There is fluorination alcohol which permuted with the fluorine a part of hydro fluorocarbon (HFC, compound which permuted a part of hydrogen of a hydrocarbon with the fluorine), hydro fluoro ether (compound which permuted a part of all hydrogen of HFE and the hydrocarbon system ether with the fluorine), and hydrogen. There is the perfluoro ether which AUSIMONT K.K. is marketing by the trade name of "GALDEN" as a compound with which the chemical formula is concretely specified among perfluoro compounds, and this compound is CF3-[(O-(CF3-) CF-CF2) n-(O-CF2) m] O-CF3. It is expressed with a chemical structure type.

[0013] Use of perfluorocarbon or the perfluoro ether is desirable as an organic solvent which contains a halogen from the field of the corrosion resistance over ozone. The solubility of the

ozone to the organic solvent containing the halogen used for this invention reaches dozens times from several times of the solubility of ozone to pure water or tap water, and purification capacity also goes up with the rise of solubility. These organic solvents are the high molecular compounds in which the monomer usually carried out the polymerization, the solubility of the ozone to the organic solvent of the same weight is as high as the case of low molecular weight, and the solubility of ozone [as opposed to the organic solvent of the same weight in the case of the amount of macromolecules] becomes low. In order to dissolve ozone content gas in this organic solvent, it is desirable to carry out like [in the usual ozone water manufacture] using a diffusion plate or an aeration ball, that is, ozone content purification liquid is easily obtained by carrying out bubbling of the ozone content gas into an organic solvent through a diffusion plate or an aeration ball.

[0014] In addition, the dissolution to ozone manufacture and an organic solvent can also be performed by one actuation. That is, if it electrolyzes using the organic solvent which installs the anode plate for ozone generating in the anode plate room of the cell divided at the anode plate room and the cathode room using the diaphragm, and contains a halogen as an anolyte, the ozone content gas generated at an anode plate room will dissolve in said organic solvent which is an anolyte as it is, and the ozone content purification liquid of this invention will be obtained. Although the ozone level of the purification liquid of this invention is dependent also on the organic solvent and temperature to be used, it is usually 300 – 500 mg/l at a room temperature, and it reaches by dozens times [several times to] the ozone level of the above-mentioned passage usual ozone water. The purification liquid which ozone content gas dissolves in the organic solvent containing the halogen of this invention, and grows into it is applicable to purification actuation of washing of precision mechanical equipments, such as sterilization of medical equipment, such as washing of electronic equipment, such as a semi-conductor, resist removal in the process which uses the lithography at the time of this electronics manufacturing, and a syringe, and a clock, washing of food, etc. as it was mentioned above.

[0015] Although it is also good to immerse this wafer in the ozone content purification liquid of this invention, since the resist which exfoliated from the wafer front face with ozone content purification liquid only in mere immersion remains in a wafer front face and the resist removal covered by the wafer front face becomes easy to check a non-exfoliated resist and contact of ozone content purification liquid, it is desirable in carrying out ultrasonic irradiation to immersion and coincidence, and promoting the desorption from the front face of an exfoliation resist. Furthermore, since the resist which exfoliated like ultrasonic irradiation is desorbed from a wafer front face even if it injects ozone content purification liquid on a revolving (spin) wafer front face and tries resist removal, processing effectiveness rises.

[0016] Moreover, the purification liquid of this invention can be used also for waste water treatment, carries out mixed shake of this oleophilic purification liquid with waste water, contacts the ozone content gas in this purification liquid to the impurity in waste water, and can perform sterilization or impurity removal. After processing becomes a bilayer and separates the purification liquid of the waste water of a hydrophilic property, and oleophilic this invention. Moreover, since the purification liquid of this invention is comparatively expensive, it is desirable to collect and carry out playback use after use, and after performing waste water treatment etc. as it is the above-mentioned, it dissociates by a decantation etc., and it performs filtration and ion-exchange-resin processing if needed.

[0017] Since it has high concentration to the extent that it does not become as compared with conventional ozone water, it has the broad application of which conventional ozone water cannot remind, an oxide skin is formed and passivated on the front face of for example, electronic equipment components, metal components, and precision components besides the above-mentioned, and it is used as an oxidizer in an organic chemistry reaction, or the purification liquid of this invention can also be used for oxidation treatment and annealing of an inorganic chemistry reaction. [raising endurance] For example, the time and effort and the risk of ozone handling of generating ozone are avoidable, reacting conventionally, the organic-acid-ized reaction which was being performed while blowing ozone into the organic solvent by the ability only reacting as a solvent using this purification liquid, if the ozone content purification liquid of

this invention is used.
[0018] In this invention, purification is called including all actuation of these and usable liquid is said to these actuation as purification liquid. Moreover, the purification actuation which uses the purification liquid of this invention may not be limited to actuation only with this purification liquid, may use together UV irradiation and the ultrasonic irradiation mentioned above, or may use gas and the liquids other than ozone for coincidence. Moreover, the solvent which does not contain an effective halogen may be used for removal of a specific component also about a solvent in addition to the organic solvent containing the above-mentioned halogen, mixing with said organic solvent to it.
[0019]
[Embodiment of the Invention] Next, although the operation gestalt of the resist removal with the ozone content purification liquid of this invention is explained based on an accompanying drawing, this invention is not limited to this. Drawing 1 is the outline front view showing 1 operation gestalt (dip coating) of the resist removal with the ozone content purification liquid concerning this invention. It is divided by the cation exchange membrane 2 which is a solid electrolyte at the anode plate room 3 and the cathode room 4, and the cathode matter powder 6 adheres to the cathode room 4 side again, respectively, and, as for the body 1 for ozone content gas making of a cell, the anode plate matter powder 5 which has the catalyst ability to the ozone content generation of gas in the anode plate room 3 side of said ion exchange membrane 2 serves as the SPE mold cell 1.
[0020] If pure water is filled in the anode plate room 3 and the cathode room 4 of this cell 1 and it energizes among two poles, the ozone content gas which is the mixed gas of ozone and oxygen in the anode plate room 3 side will occur. On the other hand, near this cell 1, the ultrasonic-cleaning tub 7 is installed and pure water 8 is filled in this washing tub 7. The wafer 11 with a resist is arranged so that the crucible 9 made from a quartz with which the base was fabricated round may be installed in this washing tub 7, and the fluorine content organic solvent 10 may be filled in this crucible 9 and it may be immersed in this organic solvent 10. The ozone content gas which occurred in the anode plate room 3 side of said cell 1 is introduced into said organic solvent 10 through a supply line 12, and is dissolved into an organic solvent 10 from aeration ball 13 front face in this organic solvent 10, and ozone content purification liquid is produced. The produced ozone content purification liquid purifies wafer 11 front face while removing the resist on a wafer 11 by the oxidizing power of the ozone and the organic solvent itself which is contacting and dissolving in the wafer 11 in this purification liquid. In this case, a supersonic wave is impressed and resist removal and the surface purification effectiveness become remarkable further.
[0021] Drawing 2 is the outline front view showing other operation gestalten (spin cleaning method) of the resist removal with the ozone content purification liquid concerning this invention, since the body 1 of a cell and its member are the same as that of drawing 1 , attaches the same sign and omits explanation. The mixed pump 14 is supplied from supply line 12a, it is mixed with organic solvent 10a stored by the depot 15 of the organic solvent containing a fluorine, and ozone content purification liquid generates the ozone content gas which occurred by the body 1 for ozone content gas making of a cell in the mixed pump 14. This ozone content purification liquid is supplied to the spin scrubber 17, after the vapor-liquid-separation tub 16 is supplied and separation removal of the non-dissolved ozone is carried out. This spin scrubber 17 has wafer 11with resist a fixed to the shaft 19 installed in the core of a saucer 18 free
[rotation].
[0022] If a comb also injects supply for ozone content purification liquid at the core of this wafer 11a, rotating wafer 11a of this spin scrubber 16, the resist in which the resist on wafer 11a exfoliated by the flux of ozone content purification liquid, and exfoliated after that will be removed from a wafer 11a front face. If rotation of a revolving shaft 19 is continued increasing remaining as it is or a rotational frequency suspending supply of ozone content purification liquid after that, and maintaining a rotational frequency, said penetrant remover of a wafer 11a front face will disperse, and desiccation of wafer 11a will be performed. After the ozone content purification liquid after use removes impurities, such as a resist mixed through the PTFE filter

20, it circulates through it to said depot 15.
[0023] (Example) Although the example of purification actuation, such as resist purification which uses the ozone content purification liquid applied to this invention next, is indicated, this example does not limit this invention.
an example 1 -- the solubility to the fluorine content organic solvent of ozone content gas was measured first. Electrolysis effective-area 90cm2 It equipped with the diaphragm made from Nafion (trade name) which is the fixed electrolyte which lead-dioxide powder is adhered to an anode plate side, and made platinum powder a cathode side adhere to a cell, respectively, and considered as the SPE mold cell, this cell was divided in the anode plate room and the cathode room by said diaphragm, and 1l. of pure water was filled in this cell. It is 100 A/dm2 to this cell. By energizing so that it may become, the mixed gas (ozone content gas) of the ozone which contains ozone 12% of the weight, and oxygen was obtained at a rate of 10g/o'clock.
[0024] It is 0.7 to the cylindrical shape scrubbing bottle made from Pyrex glass which filled FURORINATO FC-77 (97 degrees C of boiling points) 100 ml which is a fluorine content organic solvent by Sumitomo 3M, Inc. about this ozone content gas. It introduced at a rate for liter/and was made to dissolve into said organic solvent through the aeration ball made from a porosity quartz. Extract 5ml of this ozone content organic solvent, mix with 5ml of 20% of the weight of potassium iodide water solutions, and shake violently, and it is made to fully contact, and iodine ion was oxidized by ozone and made to color yellow. Next, it titrated after adding 5ml of 1/10-N sulfuric-acid water solutions and separating iodine until coloring disappeared using 1/50-N sodium-thiosulfate solution. The solution temperature of an organic solvent was changed similarly, ozone solubility was measured, respectively, and the temperature dependence of ozone solubility was investigated. The result is shown in Table 1.
[0025] Pure water was filled instead of FURORINATO FC-77 in the example of comparison 1 scrubbing bottle, ozone was dissolved on the same conditions as an example 1, and the temperature dependence of the ozone solubility to the inside of pure water was measured similarly. The result was shown all over Table 1. Table 1 shows that FURORINATO showed very high ozone solubility as compared with pure water, and high-concentration ozone content FURORINATO was obtained from the ozone content gas supplied at the temperature of 50 degrees C or less.
[0026]
[Table 1]

液温 (℃)		10	20	30	40	50
溶解度 (mg/l)	純水	83	60	49	40	34
	フロリナート	530	450	380	310	250

[0027] The resist stripper as shown in drawing 1 using the cell of example 2 example 1 was assembled. Pure water was filled to the ultrasonic-cleaning tub of this equipment, and the quartz crucible in which a top face carries out opening was further installed into this. The FURORINATO FC-77 [same] as an example 1 were put in into this crucible, and the aeration ball made from a porosity quartz has been arranged so that it may be further immersed in this FURORINATO. It lets an aeration ball pass for the ozone content gas which contains the ozone obtained in the example 1 12% of the weight, and is 0.7 in FURORINATO. It was 460 mg/l, when it supplied at a rate for liter/and the ozone level was measured after [of supply initiation] 20 minutes. It is thickness 1.2 to this ozone content FURORINATO about a positive resist TSMRV90 (TOKYO OHKA KOGYO CO., LTD. make). The 6 inch silicon wafer applied by mum was made immersed into FURORINATO. Took out after 3 minutes, it was made to dry by 120 **, and the etch rate was computed from the residual thickness of a resist by cross-section observation by SEM. The result was shown in Table 2. Ultrasonic irradiation was used together on the same conditions at the time of wafer immersion, and the etch rate was computed similarly. The result was also shown in Table 2.
[0028] The ozone levels were 60 mg/l when ozone water was produced like the example 2

except having used pure water instead of example of comparison 2 FURORINATO. The etch rate (with no ultrasonic irradiation) was computed like the example 2. The result was shown in Table 2. The table 2 showing the result of an example 2 and the example 2 of a comparison shows that a dissolution ozone level will become 7 or more times as compared with the case where pure water is a solvent if the organic solvent which contains a fluorine as a solvent of the ozone dissolution is used. It is about 2.5 when the former will be used, if the etch rate of the resist removal by ozone content purification liquid and ozone water (with no ultrasonic irradiation) is measured. A twice as many etch rate as this can be obtained, speeding up of manufacture of a wafer, as a result the semi-conductor manufacture which has this wafer can be attained, and it can respond to improvement in the speed and densification of electronics manufacturing. Furthermore, if resist removal is performed irradiating a supersonic wave, even when the same ozone content purification liquid is used, a resist removal rate will reach 4 times. This can be conjectured to be because for the resist which exfoliated from the wafer with ozone content purification liquid to flow away with purification liquid from a wafer front face with a supersonic wave and to be able to perform contact in a non-exfoliated resist and purification liquid suitably.

[0029]

[Table 2]

	オゾン含有浄化液	オゾン含有浄化液	オゾン水
液温（℃）	20	20	20
溶解オゾン濃度（mg/l）	460	460	60
超音波照射	無	有	無
ｴｯﾁﾝｸﾞ速度（μm／分）	0.1	0.4	0.04

[0030] Resist removal from a wafer with a resist was performed using the cell and spin scrubber which were shown in example 3 drawing 2 . The ozone content gas which contains ozone 12% of the weight like an example 1 was made to generate, it mixed with the FURORINATO FC-77 [same] as an example 1 with the mixed pump, the vapor-liquid-separation machine separated non-dissolved ozone, and it considered as ozone content purification liquid. When the ozone level in this ozone content purification liquid was measured, it was 460 mg/l and solution temperature was 20 degrees C.

[0031] The silicon wafer same to a spin scrubber as an example 2 was installed enabling free rotation, and it was made to rotate by 300rpm. It is said ozone content purification liquid to this revolving wafer core 0.1 It washed by injecting for 3 minutes at a rate for liter/. It is 1000rpm about the rotational frequency after suspending supply of ozone content purification liquid. It went up and spin desiccation was performed for 1 minute. Then, by cross-section observation of the wafer by SEM, residual thickness was measured and the etch rate was computed. The result was shown in Table 3.

[0032]

[Table 3]

	オゾン含有浄化液	オゾン水1	オゾン水2
液温（℃）	20	20	20
溶解オゾン濃度（mg/l）	460	60	30
ｴｯﾁﾝｸﾞ速度（μm／分）	0.4	0.2	0.1

[0033] Except having used the ozone water (ozone water 1) of 60 mg/l, the ozone level used in the example 2 of a comparison instead of example of comparison 3 ozone content purification liquid performed the same actuation as an example 3, by cross-section observation of the wafer by SEM, measured residual thickness and computed the etch rate. The result was shown in Table 3. Furthermore, the ozone water (ozone water 2) which adjusted the ozone level to 30 mg/l was produced, the wafer was washed similarly, and the etch rate was computed. The result was shown in Table 3. According to the spin cleaning method of an example 3, as compared with dip coating without the ultrasonic irradiation of an example 2, one 4 times the etch rate of this is

obtained from Table 3, and it turns out that this value has the same rate as the dip coating accompanied by ultrasonic irradiation. It can be surmised that it is because the resist which exfoliated from the wafer flows away with purification liquid from a wafer front face by rotation of a wafer and the flux of the ozone content purification liquid injected by the wafer front face and can perform contact in a non-exfoliated resist and purification liquid suitably like [this] the case of ultrasonic irradiation.

[0034] Quinoline yellow S40mg which is one sort of example 4 color was dissolved in pure-water 100 ml, ozone was mixed with FURORINATO FC-43 [10ml] (Sumitomo 3M, Inc. make and boiling point 174 **) which carried out the 440 mg/l dissolution under the room temperature, the tenebrescence of said color was observed, and the chromaticity was measured. as being shown in Table 4 -- a chromaticity -- 0.5 it was . In addition, since the chromaticity of the undiluted solution which dissolved quinoline yellow S40mg in pure-water 100 ml was too large to measure, it diluted and measured 5000 times and the chromaticity 20 was obtained.

[0035] Tenebrescence processing was similarly performed using the ozone water which carried out 60 mg/l dissolution of the ozone instead of example of comparison 4 FURORINATO FC-43, and the chromaticity after processing was measured. The result is 200 as shown in Table 4. It was 20 in twice dilution.

[0036]

[Table 4]

	オゾン含有浄化液	オゾン水	原液
液温（℃）	20	20	20
溶解オゾン濃度（mg/l）	440	60	0
エッチング速度（μm／分）	0.5	2000倍希釈で20	5000倍希釈で20

[0037] Nafion 117 which boiled the stainless steel fiber sintered compact which performed platinum plating for the titanium fiber sintered compact which performed lead-dioxide plating to example 5 front face to the anode plate and the front face in cathode and a hydrochloric acid It was used, respectively, having used the film (Du Pont make) as the electrolyte, and the cell for ozone generating was constituted. Both the electrolysis area of an anode plate and cathode is 2 5cm. It carried out. FURORINATO FC-70 (Sumitomo 3M, Inc. make and boiling point 215 **) is filled in the anode plate room of this cell, ultrapure water is added to a cathode room, and it is current density 0.5 A/dm2. Electrolysis was performed for 3 hours. The concentration of the ozone which contains the ozone level in the anode plate generating gas after 3-hour progress in FURORINATO of 10 capacity % and an anode plate room was 450 mg/l.

[0038]

[Effect of the Invention] This invention is ozone content purification liquid characterized by dissolving ozone content gas in the organic solvent containing a halogen. the organic solvent containing a halogen has alike and high ozone solubility as compared with pure water, and the ozone content purification liquid of this invention can be effectively used to washing, resist removal, etc. of the component of electronic equipment as a high concentration ozone content solution. Furthermore, since itself has a cleaning effect, the organic solvent containing a halogen can offer the purification liquid having the cleaning effect of ozone, and the cleaning effect of a solvent. Moreover, it can respond to washing of the broad class included in washing which washing in the temperature which will exceed 100 ** if the boiling point of an organic solvent is suitably chosen in this invention, although purification actuation in the temperature which exceeds 100 ** in the conventional ozone backwashing by water since the boiling point of ozone water is 100 ** could not be performed, sterilization, etc. are attained, and could not be conventionally set as the object of ozone washing, and it is responded by purification of the still more various classes other than washing or sterilization.

[0039] Moreover, if a fluorine is chosen as said halogen, performing [the purification capacity which a fluorine generally has is not only higher than other halogens, but / do not deteriorate in order that the organic solvent containing a fluorine may hardly react with ozone, continue at a

long period of time, and]-exchange and playback use is continuable. Furthermore, while purification capacity increases further that the organic solvent containing a halogen is a perfluorocarbon solvent, degradation can prevent nearly completely. Moreover, if the ozone content purification liquid of this invention is used in case it removes a resist from washing and the wafer of electronic equipment, it is effective, and the purification effectiveness which cannot be expected by accommodation of the above-mentioned fast detergency and washing temperature is acquired.

[0040] Although said ozone content purification liquid can be manufactured by blowing ozone content gas generally into the organic solvent which contains a halogen using an aeration ball, and making it dissolve, if the organic solvent which contains a halogen as an anolyte of the cell for SPE mold ozone manufacture is used as a special manufacture means, the ozone content purification liquid of this invention will be obtained at the anode plate room of this cell. A separate dissolution means becomes unnecessary by this, and workability improves. The above-mentioned resist removal can be immersed in ozone content purification liquid, and can perform a wafer, supplying or carrying out ultrasonic irradiation of the ozone content purification liquid rotating the wafer which covered the resist, and its removal effectiveness improves by any approach. This can be conjectured to be because for the resist in which the resist in which ozone content purification liquid collided with the wafer front face as flux, and exfoliated from the wafer front face was away passed from the wafer front face with purification liquid, or the supersonic wave exfoliated from the wafer front face to be passed from a wafer front face and for contact in the purification liquid of a non-exfoliated resist to be able to perform it suitably with purification liquid for last reason.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The outline front view showing 1 operation gestalt of the resist removal with the ozone content purification liquid concerning this invention.
[Drawing 2] The outline front view showing other same operation gestalten.
[Description of Notations]
1 Body of Cell
2 Ion Exchange Membrane
3 Anode Plate Room
4 Cathode Room
5 Anode Plate Matter Powder
6 Cathode Matter Powder
7 Ultrasonic-Cleaning Tub
8 Pure Water
9 Crucible
10 10a Fluorine content organic solvent
11 11a Wafer with a resist
12 12a Supply line
13 Aeration Ball
14 Mixed Pump
15 Depot
16 Vapor-Liquid-Separation Tub
17 Spin Scrubber
18 Saucer
19 Shaft
20 Filter

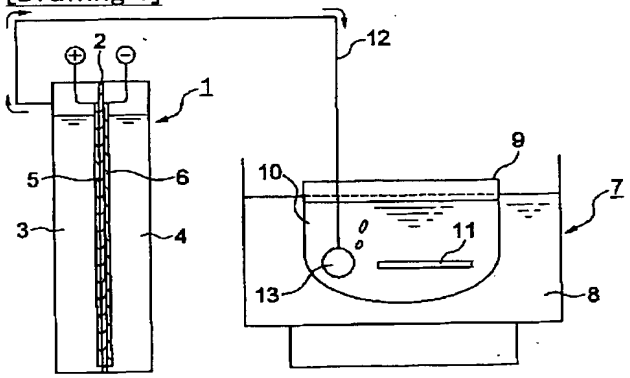
[Translation done.]

* NOTICES *

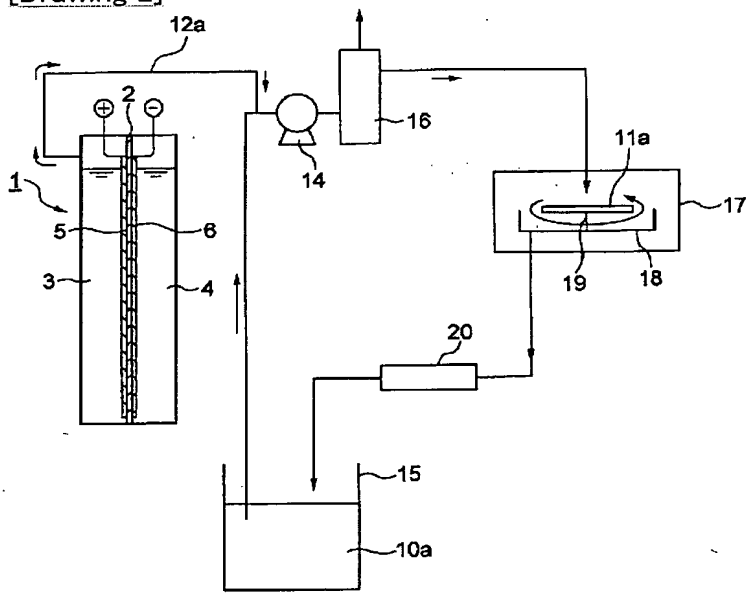
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2000－355699
（P2000－355699A）
(43)公開日　平成12年12月26日(2000.12.26)

(51)Int.Cl.⁷	識別記号	ＦＩ		テーマコード（参考）
Ｃ１１Ｄ　17/08		Ｃ１１Ｄ　17/08		４Ｈ００３
7/18		7/18		
7/50		7/50		
Ｈ０１Ｌ　21/304	６４７	Ｈ０１Ｌ　21/304	６４７Ａ	

審査請求　未請求　請求項の数８　ＯＬ　（全８頁）

(21)出願番号　特願平11－168269

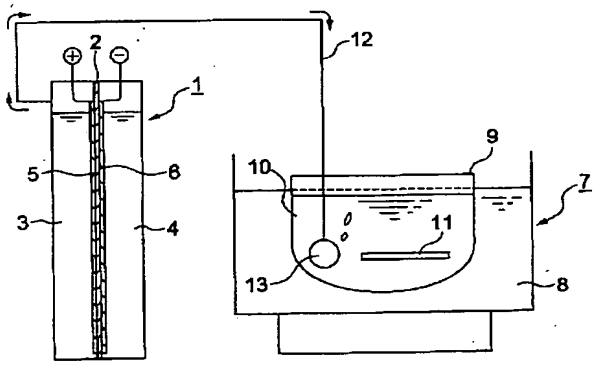
(22)出願日　平成11年６月15日(1999.6.15)

(71)出願人　390014579
ベルメレック電極株式会社
神奈川県藤沢市遠藤2023番15
(72)発明者　加藤　昌明
神奈川県横浜市旭区二俣川１－79－２、ＭＡハイツ201号
(74)代理人　100086726
弁理士　森　浩之

Ｆターム(参考)　4H003 DA14 DA15 DA17 DB03 ED19 EE03 FA27

(54)【発明の名称】　オゾン含有浄化液、その製造方法及び浄化方法

(57)【要約】
【課題】　オゾン水が電子機器洗浄用として広く利用されているが、オゾンの水に対する溶解度が低いため、高濃度オゾンによる洗浄は実施できず、高速化及び高密度化が要請される電子機器産業に十分応えることができなかった。
【解決手段】　電解槽１で生成するオゾン含有ガスをハロゲンを含有する有機溶媒10に溶解して生成するオゾン含有浄化液。オゾンの有機溶媒に対する溶解度が高いため、又ハロゲンを含有する有機溶媒自体が浄化能力を有するため、本発明の浄化液は従来のオゾン水と比較して格段の浄化能を有する。更にオゾンが水中よりも有機溶媒中で安定であるため、より長寿命の浄化液が得られる。



【特許請求の範囲】

【請求項１】　オゾン含有ガスをハロゲンを含有する有機溶媒に溶解させたことを特徴とするオゾン含有浄化液。

【請求項２】　ハロゲンがフッ素である請求項１に記載のオゾン含有浄化液。

【請求項３】　ハロゲンを含有する有機溶媒がパーフルオロカーボン溶媒である請求項１に記載のオゾン含有浄化液。

【請求項４】　電子機器洗浄及び／又はレジスト除去用である請求項１に記載のオゾン含有浄化液。

【請求項５】　オゾン含有ガスを、散気ボールを使用してハロゲンを含有する有機溶媒中に吹き込み溶解させることを特徴とするオゾン含有浄化液の製造方法。

【請求項６】　隔膜を使用して陽極室及び陰極室に区画された電解槽の陽極室にオゾン発生用陽極を設置し陽極液としてハロゲンを含有する有機溶媒を使用して電解を行い、陽極室でオゾン含有ガスを溶解したハロゲンを含有する有機溶媒を得ることを特徴とするオゾン含有浄化液の製造方法。

【請求項７】　オゾン含有ガスをハロゲンを含有する有機溶媒に溶解させたオゾン含有浄化液を、レジストが被覆された回転するウェハ表面に供給してレジストを除去することを特徴とするレジスト除去方法。

【請求項８】　オゾン含有ガスをハロゲンを含有する有機溶媒に溶解させたオゾン含有浄化液中に、超音波照射を行いながら、レジストが被覆されたウェハを浸漬してレジストを除去することを特徴とするレジスト除去方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、レジスト除去や素子の洗浄等に使用できる電子機器の洗浄液、注射器等の医療機器の殺菌液、廃水の脱色又は脱臭用の水処理用等として利用可能なオゾン含有浄化液、その製造方法及び該浄化液を使用する浄化方法に関する。

【０００２】

【従来技術】オゾンは強力でクリーンな酸化剤として注目されつつあり、特に分解生成物が酸素であり従来から使用されている塩素系のものと比較して残留物が被処理水中に残留しないこと、分解速度が速くオゾンがそれ自身残留せず二次公害の問題も全くないこと等の理由から水処理用としての使用が増加している。このように酸化剤として有用なオゾンを発生させるために従来から主として放電法及び電解法が採用され、酸素とオゾンの混合ガスであるオゾン含有ガスとして得られている。前者の放電法は放電用電極物質の混入や空気中の窒素の放電酸化物であるＮＯｘの混入があり、特に高純度を要求される電子機器洗浄用としては不適切で、他の用途としても不純物が多いため望ましくなく、現在では高純度オゾン含有ガスの製法としては実質上使用されていない。

【０００３】後者の電解法は、水の電気分解によりオゾン含有ガスを製造する方法で、この電解生成オゾン含有ガスは、水を原料とし、二酸化鉛、金、白金等を電極として使用しあるいはこれら電極物質を固体電解質（ＳＰＥ）の隔膜に付着させた構造体いわゆるＳＰＥ型電極構造体を使用して電解を行い、陽極側から水電解生成物であるオゾンを酸素との混合物として得ることができる。該電解オゾンは液体系で製造されるため完全な湿潤ガスであり、15%以上の高濃度で得られる等の特徴を有している。このオゾン含有ガスを使用して対象物の洗浄を行う場合、洗浄対象が廃水やプール水であるとオゾン含有ガスを直接洗浄対象物に吹き込んで有害不純物の分解や殺菌を行うことができる。又洗浄対象が半導体素子等の電子機器であると、電解で生成したオゾン含有ガスを純水等の高純度水に溶解してオゾン水として洗浄用に使用される（特公平８－13356 号公報）。

【０００４】前記半導体素子の製造の一工程であるシリコン基板上の微細金属配線やパターン形成工程、あるいはＬＣＤガラス基板上のパターン形成工程では、頻繁にリソグラフィー技術が用いられる。このリソグラフィーが使用される工程は、有機高分子系の感光性樹脂から成るレジストの塗布→ベイキング→マスク露光→エッチング→レジスト除去の順に行われる。前記オゾン水は、個々の半導体素子の洗浄やレジスト除去に使用され、その酸化剤としての優秀性から電子機器の素子洗浄用及びレジスト除去用として幅広く使用されている。現在では、多層配線化や線幅の狭小化等の配線の高密度化が急速に進み、製品完成までの間のリソグラフィーを使用する工程の数が増加している。現在リソグラフィーを使用する工程で使用されるレジストの除去方法としては、レジスト種専用の有機系剥離液によりレジストを溶解させる方法、酸素等のプラズマアッシングによりエッチングで除去する方法、120 ℃程度の高温高濃度硫酸と過酸化水素から成る無機系の剥離液を併用する酸化的除去方法等がある。

【０００５】このレジスト剥離後の洗浄液としては、トリクロロエチレン、１、１、１－トリクロロエタン、テトラクロロエチレン、塩化メチレン等の塩素系溶剤、フロン112 、フロン113 等のフロン系溶剤、及び芳香族系溶剤が使用されている。更にこれらの溶剤で洗浄後に、ケトン系又はアルコール性溶剤を組み合わせて洗浄を行うこともあり、例えば剥離液でレジストを剥離した後、前記塩素系溶剤又はフロン系溶剤で洗浄し、次いでメチルエチルケトン、アセトン等で洗浄し、更にイソプロパノール等で洗浄するレジスト除去方法が用いられている。

【０００６】

【発明が解決しようとする課題】現在電子機器用素子の洗浄の殆どの工程には、前述のオゾン水が使用されてい

る。該オゾン水は電解法により生成させた高純度オゾン含有ガスを使用して生成させたものであるため、電子機器洗浄に要求される純度要求に応じられる純度を有し、純度面では問題は生じていない。しかしながら洗浄対象となる電子機器の数の増加から、単なる洗浄効果の維持及び向上だけでなく、より高速度で洗浄することが望まれているが、現在のオゾン水を使用する洗浄方法では、この要望には十分に応じているとは言えない。

【０００７】又前述のレジスト除去方法は、剥離力及び洗浄力は優れているが、それぞれに取扱い上の問題点がありレジスト種に応じて使い分ける必要がある。つまりそれぞれレジスト残渣の発生、有機系廃液の発生、濃厚硫酸の発生等の問題点があり、特に近年のリソグラフィーを使用する工程の増加に伴って、廃液量が増大し、処理系統への負担増や生活環境への悪影響が危惧されている。又オゾン水によるレジスト除去あるいは洗浄方法には、①高濃度オゾン水が得られにくく、レジストのような強固な有機物の除去にはエッチングレートが小さく適切でない、②オゾンは水中では分解速度が比較的速く溶存オゾンが効果的に利用されない、③オゾン水中では温度を60℃以上に上げるとオゾンの分解速度が上昇し水蒸気圧の上昇によりオゾン濃度が下がり効果的でない、といった問題点が指摘されている。この他にも、オゾン水等をはじめとする各種浄化液による洗浄等の浄化が行われているが、より一層の浄化効果の向上が望まれている。本発明は、このような電子機器の洗浄、レジスト除去、医療機器殺菌等の各種浄化操作をより効果的にかつ不純物や廃液を発生させることなく行い得るオゾン含有浄化液、その製造方法及び該浄化液を使用する浄化方法を提供することを目的とする。

【０００８】

【課題を解決するための手段】本発明は、オゾン含有ガスをハロゲン、特にフッ素を含有する有機溶媒に溶解させたことを特徴とするオゾン含有浄化液であり、該浄化液は電子機器洗浄及び／又はレジスト除去用として好適である。この浄化液は、オゾン含有ガスを、散気ボールを使用してハロゲンを含有する有機溶媒中に吹き込み溶解させることにより、又はハロゲンを含有する有機溶媒を陽極液として使用するオゾンの電解生成により製造できる。又該浄化液を使用するスピン洗浄法又は超音波照射を伴う浸漬法により効率良く製造できる。

【０００９】以下本発明を詳細に説明する。本発明に係る、オゾン含有ガスをハロゲンを含有する有機溶媒に溶解させて成るオゾン含有浄化液は次のような特徴を有している。

①　オゾンの有機溶媒に対する溶解度が水に対する溶解度より格段に高いため、浄化液特に洗浄液として洗浄能力が高くなる。

②　ハロゲンを含有する有機溶媒自体にも浄化能力があるため、更に一層の浄化能力の向上が達成できる。

③　有機溶媒の選択、特に沸点を好適に選択すると、オゾン水では行い得ない100 ℃を越える温度での洗浄や殺菌等が可能になり、従来はオゾン洗浄の対象となりえなかった洗浄を含む幅広い種類の洗浄に対応でき、更に洗浄や殺菌以外の多様な種類の浄化に応じられる。

④　有機溶媒中でのオゾン分解が水中でのオゾン分解より進行しにくいため、浄化液としての寿命が長くなる。

【００１０】本発明で使用可能なハロゲンを含有する有機溶媒のハロゲンとしてはフッ素、塩素、臭素及び沃素があり、中でもフッ素及び塩素の使用が望ましく、フッ素の使用が最適である。本発明のハロゲンを含有する有機溶媒としてフッ素を含む有機溶媒、特にパーフルオロカーボン化合物の溶媒が好ましいのは、フッ素を含む有機溶媒は殆どオゾンと反応せず、対象浄化物の処理工程中に安定に維持され、再生等を行うことなく繰り返し使用できるからであり、パーフルオロカーボン化合物を使用すると一層の耐性向上が達成できる。塩素、臭素あるいは沃素を含有する有機溶媒の中にはオゾンと反応して分解したり劣化したりする溶媒があり、分解物による汚染も考えられるため、フッ素以外のハロゲンを含有する有機溶媒を使用する場合にはオゾンとの反応性を考慮して選択する必要がある。

【００１１】更に本発明の有機溶媒は、室温付近で液体であることが望ましく、例えば沸点が30℃以上、融点が20℃以下の有機溶媒であることが好ましい。沸点が100 ℃を越える有機溶媒を選択すると前述の通りオゾン水では不可能な温度での洗浄等が可能になり、従来のオゾン処理では成し得なかった高度の洗浄を必要とする部材の洗浄等の浄化操作が可能になる。該有機溶媒は単独の化合物でも混合物でも良く、２種以上のハロゲンを含んでいても良い。所望の沸点の有機溶媒が見出せない場合には２以上の有機溶媒を混合して見掛け上の沸点を調節することができる。

【００１２】本発明の有機溶媒、特にフッ素を含有する有機溶媒としては、パーフルオロカーボン（ＰＦＣ、炭化水素の全ての水素をフッ素で置換した化合物）、パーフルオロエーテル（ＰＦＥ、炭化水素系エーテルの全ての水素をフッ素で置換した化合物）、ハイドロクロロフルオロカーボン（ＨＣＦＣ、炭化水素の水素の一部を塩素及びフッ素で置換した化合物）、ハイドロフルオロカーボン（ＨＦＣ、炭化水素の水素の一部をフッ素で置換した化合物）、ハイドロフルオロエーテル（ＨＦＥ、炭化水素系エーテルの全ての水素の一部をフッ素で置換した化合物）及び水素の一部をフッ素で置換したフッ素化アルコール等がある。パーフルオロ化合物のうち、具体的に化学式が特定されている化合物としてアウジモント社が「ＧＡＬＤＥＮ」という商品名で市販しているパーフルオロエーテルがあり、この化合物は、$CF_3-[(O-(CF_3-)CF-CF_2)_n-(O-CF_2)_m]O-CF_3$ の化学構造式で表される。

【００１３】オゾンに対する耐食性という面からは、ハロゲンを含有する有機溶媒としてパーフルオロカーボンやパーフルオロエーテルの使用が望ましい。本発明に使用するハロゲンを含有する有機溶媒に対するオゾンの溶解度は、純水や水道水に対するオゾンの溶解度の数倍から数十倍に達し、溶解度の上昇に伴って浄化能力も上昇する。これらの有機溶媒は通常モノマーが重合した高分子化合物で、低分子量の場合ほど同一重量の有機溶媒に対するオゾンの溶解度は高く、高分子量の場合ほど同一重量の有機溶媒に対するオゾンの溶解度は低くなる。該有機溶媒にオゾン含有ガスを溶解させるには、通常のオゾン水製造の場合のように散気板や散気ボールを使用して行うことが望ましく、つまりオゾン含有ガスを散気板や散気ボールを通して有機溶媒中にバブリングすることにより容易にオゾン含有浄化液が得られる。

【００１４】この他に、オゾン製造と有機溶媒への溶解を一回の操作で行うこともできる。つまり隔膜を使用して陽極室及び陰極室に区画された電解槽の陽極室にオゾン発生用陽極を設置し、かつ陽極液としてハロゲンを含有する有機溶媒を使用して電解を行うと陽極室で生成するオゾン含有ガスがそのまま陽極液である前記有機溶媒に溶解して本発明のオゾン含有浄化液が得られる。本発明の浄化液のオゾン濃度は、使用する有機溶媒や温度にも依存するが通常室温で300 ～500 mg/lであり、前述の通り通常のオゾン水のオゾン濃度の数倍～数十倍に達する。本発明のハロゲンを含有する有機溶媒にオゾン含有ガスが溶解させて成る浄化液は、前述した通り、半導体等の電子機器の洗浄、該電子機器製造時のリソグラフィーを使用する工程におけるレジスト除去、注射器等の医療機器の殺菌、時計等の精密機器の洗浄、食品の洗浄等の浄化操作に使用できる。

【００１５】ウェハ表面に被覆されたレジスト除去は、単に該ウェハを本発明のオゾン含有浄化液に浸漬するだけでも良いが、単なる浸漬だけではオゾン含有浄化液によりウェハ表面から剥離されたレジストがウェハ表面に残って未剥離のレジストとオゾン含有浄化液の接触を阻害しやすくなるため、浸漬と同時に超音波照射して剥離レジストの表面からの脱離を促進することが好ましい。更に回転（スピン）しているウェハ表面にオゾン含有浄化液を噴射してレジスト除去を試みても、超音波照射と同様に剥離したレジストがウェハ表面から脱離するため、処理効率が上昇する。

【００１６】又本発明の浄化液は廃水処理にも使用でき、親油性の該浄化液を廃水と混合震盪して本浄化液中のオゾン含有ガスを廃水中の不純物と接触させて殺菌あるいは不純物除去を行える。処理後は親水性の廃水と親油性の本発明の浄化液は二層になって分離する。又本発明の浄化液は比較的高価であるため使用後に回収し再生使用することが望ましく、前述の通り廃水処理等を行った後はデカンテーション等で分離し、必要に応じて濾過やイオン交換樹脂処理を行う。

【００１７】本発明の浄化液は、従来のオゾン水とは比較にならないほどの高濃度を有するため従来のオゾン水では想起し得ない幅広い用途を有し、前述以外にも例えば電子機器部品、金属部品、精密部品の表面に酸化被膜を形成して不動態化して、耐久性を向上させたり、有機化学反応における酸化剤として使用したり、無機化学反応の酸化処理やアニーリングに使用することも可能である。例えば従来は有機溶媒中にオゾンを吹き込みながら行っていた有機酸化反応を、本発明のオゾン含有浄化液を使用すると単に該浄化液を溶媒として使用して反応を行うことができ、反応を行いながらオゾンを発生させる手間やオゾン取扱いの危険を回避できる。

【００１８】本発明ではこれら全ての操作を含めて浄化と称し、これらの操作に使用可能な液を浄化液という。又本発明の浄化液を使用する浄化操作はこの浄化液のみによる操作に限定されず、例えば紫外線照射や前述した超音波照射を併用し、あるいはオゾン以外のガスや液体を同時に使用しても良い。又溶剤についても前述のハロゲンを含有する有機溶媒以外に特定の成分の除去に効果のあるハロゲンを含有しない溶媒を前記有機溶媒と混合して使用しても良い。

【００１９】

【発明の実施の形態】次に添付図面に基づいて本発明のオゾン含有浄化液によるレジスト除去の実施形態を説明するが、本発明はこれに限定されるものではない。図１は本発明に係るオゾン含有浄化液によるレジスト除去の一実施形態（浸漬法）を示す概略正面図である。オゾン含有ガス製造用電解槽本体１は、固体電解質である陽イオン交換膜２により陽極室３と陰極室４に区画され、前記イオン交換膜２の陽極室３側にはオゾン含有ガス発生に対する触媒能を有する陽極物質粉末５が、又陰極室４側には陰極物質粉末６がそれぞれ付着してＳＰＥ型電解槽１となっている。

【００２０】この電解槽１の陽極室３及び陰極室４に純水を満たし両極間に通電すると、陽極室３側でオゾンと酸素の混合ガスであるオゾン含有ガスが発生する。一方この電解槽１の近傍には、超音波洗浄槽７が設置され、該洗浄槽７内には純水８が満たされている。この洗浄槽７内に、底面が丸く成形された石英製るつぼ９が設置され、該るつぼ９中にはフッ素含有有機溶媒10が満たされかつ該有機溶媒10に浸漬するようにレジスト付ウェハ11が配置されてる。前記電解槽１の陽極室３側で発生したオゾン含有ガスは供給ライン12を通って前記有機溶媒10中に導入され、該有機溶媒10中の散気ボール13表面から有機溶媒10中に溶解し、オゾン含有浄化液が作製される。作製されたオゾン含有浄化液は該浄化液中のウェハ11に接触し溶解しているオゾン及び有機溶媒自身の酸化力によりウェハ11上のレジストを除去するとともにウェハ11表面を浄化する。この際に超音波が印加され、更に

レジスト除去及び表面浄化効果が顕著になる。

【００２１】図２は本発明に係るオゾン含有浄化液によるレジスト除去の他の実施形態（スピン洗浄法）を示す概略正面図であり、電解槽本体１及びその部材は図１と同様であるため同一符号を付して説明を省略する。オゾン含有ガス製造用電解槽本体１で発生したオゾン含有ガスは供給ライン12ａから混合ポンプ14に供給され、フッ素を含有する有機溶媒の貯留槽15に貯留された有機溶媒10ａと混合され、混合ポンプ14中でオゾン含有浄化液が生成する。このオゾン含有浄化液は気液分離槽16に供給され、未溶解オゾンが分離除去された後、スピン洗浄器17に供給される。このスピン洗浄器17は、受皿18の中心に回転自在に設置された軸19に固定されたレジスト付ウェハ11ａを有している。

【００２２】このスピン洗浄器16のウェハ11ａを回転させながらオゾン含有浄化液を該ウェハ11ａの中心に供給もくしは噴射すると、ウェハ11ａ上のレジストがオゾン含有浄化液の流束により剥離し、その後剥離したレジストはウェハ11ａ表面から除去される。その後オゾン含有浄化液の供給を停止しかつ回転数を維持したままそのまま又は回転数を増加しながら回転軸19の回転を継続すると、ウェハ11ａ表面の前記洗浄液が飛散してウェハ11ａの乾燥が行われる。使用後のオゾン含有浄化液はＰＴＦＥフィルター20を通して混入したレジスト等の不純物を除去した後、前記貯留槽15に循環される。

【００２３】（実施例）次に本発明に係るオゾン含有浄化液を使用するレジスト浄化等の浄化操作の実施例を記載するが、該実施例は本発明を限定するものではない。

実施例１

まずオゾン含有ガスのフッ素含有有機溶媒への溶解度を測定した。電解有効面積90cm² の電解槽に、陽極面に二酸化鉛粉末を、陰極面に白金粉末をそれぞれ付着させた固定電解質であるナフィオン（商品名）製隔膜を装着してＳＰＥ型電解槽とし、前記隔膜により該電解槽を陽極室と陰極室に区画し、該電解槽内には純水１リットルを満たした。この電解槽に100 A/dm² となるように通電することにより、オゾンを12重量％含有するオゾンと酸素の混合ガス（オゾン含有ガス）が10ｇ／時の割合で得られた。

【００２４】このオゾン含有ガスを、住友スリーエム株式会社製のフッ素含有有機溶媒であるフロリナートＦＣ－77（沸点97℃）100 ｍlを満たしたパイレックスガラス製の円筒形ガス洗浄瓶に0.7 リットル／分の割合で導入し、多孔質石英製の散気ボールを通して前記有機溶媒中に溶解させた。このオゾン含有有機溶媒５ｍlを採取し、20重量％の沃化カリウム水溶液５ｍlと混合しかつ激しく震盪して十分に接触させて、沃素イオンをオゾンにより酸化させて黄色く発色させた。次に1/10Ｎ硫酸水溶液５ｍlを添加して沃素を遊離させた後、1/50Ｎチオ硫酸ナトリウム溶液を用いて発色が消えるまで滴定を行った。同様にして有機溶媒の液温を変えてそれぞれオゾン溶解度を測定してオゾン溶解度の温度依存性を調べた。その結果を表１に示す。

【００２５】比較例１

ガス洗浄瓶中にフロリナートＦＣ－77の代わりに純水を満たし、実施例１と同一条件でオゾンを溶解させ、同様にして純水中へのオゾン溶解度の温度依存性を測定した。その結果を表１中に示した。表１から、フロリナートは純水と比較して極めて高いオゾン溶解性を示し、50℃以下の温度では供給したオゾン含有ガスより高濃度のオゾン含有フロリナートが得られたことが分かる。

【００２６】

【表１】

液温（℃）		10	20	30	40	50
溶解度（mg/l）	純水	83	60	49	40	34
	フロリナート	530	450	380	310	250

【００２７】実施例２

実施例１の電解槽を使用して図１に示すようなレジスト除去装置を組み立てた。この装置の超音波洗浄槽に純水を満たし、更にこの中に上面が開口する石英るつぼを設置した。このるつぼ中に実施例１と同じフロリナートＦＣ－77を入れ、更にこのフロリナートに浸漬するように多孔質石英製の散気ボールを配置した。実施例１で得たオゾンを12重量％含むオゾン含有ガスを散気ボールを通してフロリナート中に0.7 リットル／分の割合で供給し、供給開始20分後にオゾン濃度を測定したところ460 mg/lであった。このオゾン含有フロリナートにポジ型レジストＴＳＭＲＶ90（東京応化工業株式会社製）を厚さ1.2 μｍで塗布した６インチシリコンウェハをフロリナート中に浸漬させた。３分後に取り出して120 ℃で乾燥させ、ＳＥＭによる断面観察により、レジストの残留膜厚からエッチング速度を算出した。その結果を表２に示した。同じ条件でウェハ浸漬時に超音波照射を併用して、同様にしてエッチング速度を算出した。その結果も表２に示した。

【００２８】比較例２

フロリナートの代わりに純水を使用したこと以外は実施例２と同様にしてオゾン水を作製したところオゾン濃度は60mg/lであった。実施例２と同様にして（超音波照射なし）エッチング速度を算出した。その結果を表２に示した。実施例２及び比較例２の結果を示す表２から、オゾン溶解の溶媒としてフッ素を含有する有機溶媒を使用

すると、純水が溶媒の場合と比較して溶解オゾン濃度が７倍以上になることが分かる。オゾン含有浄化液とオゾン水（超音波照射なし）によるレジスト除去のエッチング速度を比較すると前者を使用すると約2.5 倍のエッチング速度が得られ、ウェハの製造、ひいては該ウェハを有する半導体製造の迅速化が達成でき、電子機器製造の高速化及び高密度化に対応できる。更に超音波を照射しながらレジスト除去を行うと、同じオゾン含有浄化液を使用した場合でもレジスト除去速度は４倍に達する。これはオゾン含有浄化液によりウェハから剥離したレジストが超音波によりウェハ表面から浄化液とともに流れ去り、未剥離レジストと浄化液との接触を好適に行い得るからであると推測できる。

【００２９】

【表２】

	オゾン含有浄化液	オゾン含有浄化液	オゾン水
液温（℃）	20	20	20
溶解オゾン濃度（mg/l）	460	460	60
超音波照射	無	有	無
ｴｯﾁﾝｸﾞ 速度（μm／分）	0.1	0.4	0.04

【００３０】実施例３

図２に示した電解槽及びスピン洗浄器を使用してレジスト付ウェハからのレジスト除去を行った。実施例１と同様にしてオゾンを12重量％含むオゾン含有ガスを生成させ、混合ポンプにより実施例１と同じフロリナートＦＣ－77と混合し、気液分離器で未溶解オゾンを分離してオゾン含有浄化液とした。このオゾン含有浄化液中のオゾン濃度を測定したところ、460 mg/lであり、液温は20℃であった。

【００３１】スピン洗浄器に実施例２と同じシリコンウェハを回転自在に設置し、300rpmで回転させた。この回転しているウェハ中心に前記オゾン含有浄化液を0.1 リットル／分の割合で３分間噴射して洗浄を行った。オゾン含有浄化液の供給を停止した後、回転数を1000rpm に上昇して１分間スピン乾燥を行った。その後、ＳＥＭによるウェハの断面観察により、残留膜厚を測定しエッチング速度を算出した。その結果を表３に示した。

【００３２】

【表３】

	オゾン含有浄化液	オゾン水１	オゾン水２
液温（℃）	20	20	20
溶解オゾン濃度（mg/l）	460	60	30
ｴｯﾁﾝｸﾞ 速度（μm／分）	0.4	0.2	0.1

【００３３】比較例３

オゾン含有浄化液の代わりに比較例２で使用したオゾン濃度は60mg/lのオゾン水（オゾン水１）を使用したこと以外は実施例３と同じ操作を行い、ＳＥＭによるウェハの断面観察により、残留膜厚を測定しエッチング速度を算出した。その結果を表３に示した。更にオゾン濃度を30mg/lに調整したオゾン水（オゾン水２）を作製し、同様にウェハの洗浄を行い、エッチング速度を算出した。その結果を表３に示した。表３から実施例３のスピン洗浄法によると実施例２の超音波照射のない浸漬法と比較して４倍のエッチング速度が得られ、この値は超音波照射を伴う浸漬法と同じ速度があることが分かる。これも超音波照射の場合と同じように、ウェハから剥離したレジストがウェハの回転とウェハ表面に噴射されるオゾン含有浄化液の流束によりウェハ表面から浄化液とともに流れ去り、未剥離レジストと浄化液との接触を好適に行い得るからであると推測できる。

【００３４】実施例４

染料の１種であるキノリンイエローＳ40mgを純水100 ml に溶解し、室温下でオゾンを440 mg/l溶解した10mlのフロリナートＦＣ－43（住友スリーエム株式会社製、沸点174 ℃）と混合し、前記染料の褪色を観察し色度を測定した。表４に示す通り、色度は0.5 であった。なおキノリンイエローＳ40mgを純水100 ml に溶解した原液の色度は大き過ぎて測定できなかったため、5000倍に希釈し測定し、色度20が得られた。

【００３５】比較例４

フロリナートＦＣ－43の代わりにオゾンを60mg/l溶解したオゾン水を使用して同様に褪色処理を行い、処理後の色度を測定した。その結果は表４に示す通り、200 倍希釈で20であった。

【００３６】

【表４】

	オゾン含有浄化液	オゾン水	原液
液温（℃）	20	20	20
溶解オゾン濃度（mg/l）	440	60	0
ｴｯﾁﾝｸﾞ 速度（μm／分）	0.5	2000倍希釈で20	5000倍希釈で20

【００３７】実施例５

表面に二酸化鉛めっきを施したチタン繊維焼結体を陽極、表面に白金めっきを施したステンレス繊維焼結体を陰極、塩酸中で煮沸したナフィオン117 （デュポン社製）膜を電解質として、それぞれ用いてオゾン発生用電解槽を構成した。陽極及び陰極の電解面積は共に５cm^2とした。この電解槽の陽極室にフロリナートＦＣ－70（住友スリーエム株式会社製、沸点215 ℃）を満たし、陰極室には超純水を加え、電流密度0.5 A/dm^2 で３時間電解を行った。３時間経過後の陽極発生ガス中のオゾン濃度は10容量％、陽極室のフロリナートに含有されるオゾンの濃度は450 mg/lであった。

【００３８】

【発明の効果】本発明は、オゾン含有ガスをハロゲンを含有する有機溶媒に溶解させたことを特徴とするオゾン含有浄化液である。ハロゲンを含有する有機溶媒は純水と比較してオゾン溶解度が格段に高く、本発明のオゾン含有浄化液は高濃度オゾン含有溶液として、電子機器の素子の洗浄やレジスト除去等に効果的に使用できる。更にハロゲンを含有する有機溶媒はそれ自身が浄化作用を有するため、オゾンの浄化作用と溶媒の浄化作用を合わせ持つ浄化液が提供できる。又オゾン水は沸点が100 ℃であるため、従来のオゾン水洗浄では100 ℃を越える温度での浄化操作は行い得なかったが、本発明では有機溶媒の沸点を好適に選択すると、100 ℃を越える温度での洗浄や殺菌等が可能になり、従来はオゾン洗浄の対象となりえなかった洗浄を含む幅広い種類の洗浄に対応でき、更に洗浄や殺菌以外の多様な種類の浄化に応じられる。

【００３９】又前記ハロゲンとしてフッ素を選択すると、一般的にフッ素の有する浄化能力は他のハロゲンより高いだけでなく、フッ素を含有する有機溶媒は殆どオゾンと反応しないため劣化することがなく、長期間に亘って交換や再生を行うこと使用を継続できる。更にハロゲンを含有する有機溶媒がパーフルオロカーボン溶媒であると更に浄化能力が高まるとともに、劣化がほぼ完全に防止できる。又本発明のオゾン含有浄化液は、電子機器の洗浄やウェハからレジストを除去する際に使用すると効果的で、前述の飛躍的洗浄力及び洗浄温度の調節により予期できない浄化効果が得られる。

【００４０】前記オゾン含有浄化液は、一般的にはオゾン含有ガスを、散気ボールを使用してハロゲンを含有する有機溶媒中に吹き込み溶解させることにより製造できるが、特殊な製造手段として、ＳＰＥ型オゾン製造用電解槽の陽極液としてハロゲンを含有する有機溶媒を使用すると、該電解槽の陽極室で本発明のオゾン含有浄化液が得られる。これにより別個の溶解手段が不要になり、作業性が向上する。前述のレジスト除去は、レジストを被覆したウェハを回転させながらオゾン含有浄化液を供給し、あるいは超音波照射しながらウェハをオゾン含有浄化液に浸漬して行うことができ、いずれの方法でも除去効率が向上する。これはオゾン含有浄化液が流束としてウェハ表面と衝突してウェハ表面から剥離したレジストを浄化液とともにウェハ表面から流し去り、あるいは超音波がウェハ表面から剥離したレジストを浄化液とともにウェハ表面から流し去るため、未剥離レジストの浄化液との接触が好適に行い得るからであると推測できる。

【図面の簡単な説明】

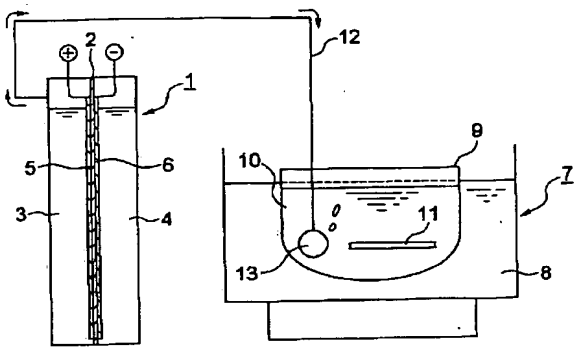
【図１】本発明に係るオゾン含有浄化液によるレジスト除去の一実施形態を示す概略正面図。

【図２】同じく他の実施形態を示す概略正面図。

【符号の説明】

1　電解槽本体
2　イオン交換膜
3　陽極室
4　陰極室
5　陽極物質粉末
6　陰極物質粉末
7　超音波洗浄槽
8　純水
9　るつぼ
10、10ａ　フッ素含有有機溶媒
11、11ａ　レジスト付ウェハ
12、12ａ　供給ライン
13　散気ボール
14　混合ポンプ
15　貯留槽
16　気液分離槽
17　スピン洗浄器
18　受皿
19　軸
20　フィルター

【図１】



【図２】